

AD-A049 873

UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT O--ETC F/G 7/2
RATE OF PRIMARY PHOTOPRODUCT FORMATION FOR AQUEOUS TRIS(ETHYLEN--ETC(U)
DEC 77 A W ADAMSON, R T WALTERS, R FUKUDA N00014-76-C-0548

UNCLASSIFIED

TR-3

NL

| OF |
AD
A049873



END
DATE
FILMED
3 - 78
DDC



AD A 049873

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0548

TECHNICAL REPORT NO. 3

12
B S

Rate of Primary Photoproduct Formation for Aqueous
Tris(ethylenediamine) Chromium(III).

by

A. W. Adamson, R. T. Walters, R. Fukuda, and A. R. Gutierrez

Prepared for Publication

in the

Journal of the American Chemical Society

Department of Chemistry
University of Southern California
Los Angeles, California 90007

December, 1977

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

Approved for Public Release; Distribution Unlimited.

DDC
RECEIVED
FEB 13 1978
RECEIVED
D

AD No. 1
JDC FILE COPY

14. REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 7R-3	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9	
4. TITLE (and Subtitle) Rate of Primary Photoproduct Formation for Aqueous Tris(ethylenediamine) Chromium(III).		5. TYPE OF REPORT & PERIOD COVERED Technical Report, No. 3, 1977.	
6. PERFORMING ORG. REPORT NUMBER		7. AUTHOR(s) A. W. Adamson, R. T. Walters, R. Fukuda, and A. R. Gutierrez	
8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0548 NSF-CHE74-08535		9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Department of Chemistry Los Angeles, California 90007	
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-609		11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 472) Arlington, Va. 22217	
12. REPORT DATE December 1977		13. NUMBER OF PAGES 9	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 14p.		15. SECURITY CLASS. (of this report) Unclassified	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		ACCESSION FOR DTIC <input checked="" type="checkbox"/> White Section DDC <input type="checkbox"/> Buff Section UNANNOUNCED <input type="checkbox"/> JUSTIFICATION..... BY..... DISTRIBUTION/AVAILABILITY CODES Dist. AVAIL. and/or SPECIAL A	
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) photochemistry coordination compounds laser pulse photolysis tris(ethylenediamine) Cr(III)			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The appearance of primary photoproduct is observed by monitoring a solution, following pulse photolysis at 530 nm, using a high energy 20 nsec laser pulse. Sixty percent of the product formation follows the lifetime of the first doublet thexi state; the remaining is prompt and attributed to reaction from the first quartet thexi state.			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

361 555

LB

Rate of Primary Photoproduct Formation for Aqueous
Tris(ethylenediamine) Chromium(III).

A. W. Adamson*, R. T. Walters, R. Fukuda, and A. R. Gutierrez[†].

[Department of Chemistry, University of Southern California, Los Angeles,
California, 90007]

[†] Present address: I.B.M., 5600 Cottle Road, San Jose, California 95193.

Sir:

We report here what we believe to be the first direct measurement of the rate of primary photoproduct formation for a Cr(III) coordination compound. The experiment is one of monitoring the rate of absorbance change, following excitation at 530 nm by a high intensity, 20 nsec laser pulse; see Figure 1.

Aqueous Cr(en)_3^{3+} (at pH 2) was chosen as the initial system because of the wealth of other information available. The photochemistry has been studied in detail;^[1] aquation occurs with quantum yield $\phi = 0.37$ around 25°C, the primary product being $\text{Cr(en)}_2(\text{enH})(\text{H}_2\text{O})^{4+}$ ^[2]. Emission from the first thexi doublet state, D_1° , has been observed^[3] and its lifetime measured in room temperature solution^[4]. In addition, emission quenching studies have shown that 50-60% of ϕ is quenched on extensive quenching of emission (with 1.5 M Co^{2+} or Fe^{2+} ions^[5] or 0.1 M OH^- ions^[6]). The general mechanistic picture is shown in Figure 2. Excitation produces a Franck-Condon manifold, Q_{FC} , which thermally equilibrates rapidly to the first thexi quartet state, Q_1° . Intersystem crossing to D_1° appears to be prompt, that is, to occur before complete thermal equilibration^[7].

The most direct interpretation of the emission quenching results is certainly that some 50-60% of photoreaction occurs via D_1^0 , with the rest from Q_1^0 . However, the required quencher concentrations are sufficiently high that simple mass action kinetics may not be valid, and it is difficult absolutely to rule out the possibility that the effect includes some static or even dynamic Q_1^0 quenching. The question has been complicated by not knowing whether intersystem crossing is prompt or only through Q_1^0 , nor what the lifetime of Q_1^0 is.

The present line of investigation was undertaken as a means of determining lifetimes of reactive excited states directly, that is, through the rate at which they produce primary photoproducts. As a minimum, in the present case, we expected to gain information on the unknown Q_1^0 lifetime; we might also be able to test or add to inferences from the emission results.

Our typical result is indicated in Figure 1, which includes a copy of an actual oscilloscope photograph. The 20 nsec excitation pulse, shown by one of the sweeps of the dual beam oscilloscope, calibrates the pulse energy for that experiment. The second sweep, usually with another time base, follows the monitoring beam intensity. When monitoring at 580 nm, there is a prompt increase in absorbance (which follows the excitation pulse in rate of appearance), followed by a slower increase of about 1 μ sec grow-in time; no further change in absorbance occurs out to at least 200 μ sec. Excited state absorption is ruled out since the increased absorption is permanent. We can, further, identify the absorbance change as due to primary photoproduct formation. The expected spectral change is that of a red shift of the first ligand field (L_1) absorption band^[2]. We find the total absorbance increase to be about that calculated for the expected amount of photolysis (ca 5% in the monitored zone of solution). Monitoring at other wavelengths gives

results consistent with the difference spectrum between Cr(en)_3^{3+} and the photoproduct--including wave-lengths at which decreased rather than increased absorption should occur.

The slower or delayed photoproduct appearance is definitely coupled with D_1° . The grow-in is exponential, and, as shown in Figure 3, the rate constants agree with those for D_1° emission (determined in parallel experiments to the monitored ones). We assign this component of reaction to D_1° .

The prompt absorbance increase must therefore be due to reaction from Q_1° . We can thus conclude that the lifetime of Q_1° is less than 20 nsec. The ratio, R , of the delayed to the prompt increase in optical density (at 580 nm) is 2.35 (essentially independent of temperature). Analysis gives

$$R = \frac{\phi_D(\gamma - 1) + f_{isc}}{\phi_Q(\gamma - 1) - f_{isc}} \quad (1)$$

where ϕ_D and ϕ_Q are the partial quantum yields associated with D_1° and Q_1° ($\phi_D + \phi_Q = \phi$), γ is the product to reactant extinction coefficient ratio and f_{isc} is the intersystem crossing efficiency. The presence of the f_{isc} terms is a consequence of allowing for ground state bleaching. We find γ to be ca 40 at 580 nm⁹; the f_{isc} terms are therefore almost negligible and Eq. (1) gives $\phi_D/\phi = 66\text{--}69\%$. We conclude that about two thirds of photoproduct formation occurs from or through D_1° .

The above figure is somewhat, but perhaps not seriously, higher than the estimates from quantum yield quenching studies^{5b,6}. It was, of course, desirable to determine the effect of known quenchers on our prompt and delayed absorbance changes. At the high quencher concentrations needed,

however, the monitoring transients became quite complex--we suspect additional chemistry to simple quenching, and are pursuing both this aspect and the behavior of other Cr(III) amines. The present results confirm, however, that D_1° is indeed the rate controlling precursor to a majority of the photoreaction, and set a maximum lifetime for Q_1° , the other producer of photoproduct.

Acknowledgements

These investigations have been supported in part by Office of Naval Research Contract N00014-76-C-0548, with National Science Foundation Grant CHE 74-08535 to the University of Southern California. The valuable contributions of A. Remeikas in the design of the detection software is gratefully acknowledged.

References

1. See E. Zinato, "Concepts of Inorganic Photochemistry," A. W. Adamson and P. D. Fleischauer, eds., Wiley, New York, 1975.
2. W. Geiss and H. L. Schl  fer, Z. Anorg. Allgem. Chem., 271, 115 (1953).
3. N. A. P. Kane-Maguire and C. H. Langford, Chem. Comm., 895 (1971).
4. (a) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, J. Amer. Chem. Soc., 93, 339 (1971). (b) W. Geis, H. F. Wasgestian, and H. Kelm, Ber. Bunsenges. Phys. Chem., 76, 1093 (1972). (c) A. W. Adamson, C. Geosling, R. Pribush, and R. Wright, Inorg. Chim. Acta, 16, L5 (1976).
5. (a) H. F. Wasgestian, R. Ballardini, G. Varani, L. Moggi, and V. Balzani, J. Phys. Chem., 77, 2614 (1973). (b) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, J. Phys. Chem., 77, 2947 (1973).
6. N. A. P. Kane-Maguire, J. E. Phifer, and C. G. Toney, Inorg. Chem., 15, 593 (1976).

7. See Ref. 6 and citations therein. In addition, we see emission from D_1^0 within about 3 nsec of 530 nm excitation. A yet higher rate of appearance of D_1^0 is found for various Cr(III) thiocyanato complexes (D. Kirk, E. Hoggard, G. B. Porter, M. G. Rockley, and M. W. Windsor, Chem. Phys. Letters, 37, 199 (1976)), for which D_1^0 absorption was reported to occur within short psec following excitation. We agree that such rapid appearance of D_1^0 can be attributed to $Q_1^0 \rightarrow D_1^0$, but believe that various other results (see also Ref. 8) make the prompt process the more likely one.
8. F. Castelli and L. S. Forster, J. Phys. Chem., 81, 403 (1977).
9. The value of γ was obtained in two ways. The spectra of solutions of $Cr(en)_3^{3+}$ was determined for successive degrees of photolysis at 515 nm by means of an Ar ion laser, and the degree of photolysis determined from the changes around 450 nm, using extinction coefficients, ϵ_p , for $Cr(en)_2(enH)(H_2O)^{4+}$ reported in Ref. 10. Our spectra, which were extended to the 580 nm region, gave the extinction coefficient for the reactant $Cr(en)_3^{3+}$ as $0.08 \pm 0.01 \text{ M}^{-1} \text{ cm}^{-1}$ at 580 nm, and, from the calculated degrees of reaction in the successive photolyses, ϵ_p as $3.3 \text{ M}^{-1} \text{ cm}^{-1}$, or $\gamma = \text{ca } 40$. In addition, Sephadex chromatography of the photolyzed solution yielded an orange fraction having the reported¹⁰ ϵ_p of $55 \text{ M}^{-1} \text{ cm}^{-1}$ at the band maximum at 475 nm. The directly measured ϵ_p at 580 nm was again $3.3 \text{ M}^{-1} \text{ cm}^{-1}$. All solutions were filtered through a Millipore filter prior to spectrophotometry since traces of dust can add substantially to the absorption of weakly absorbing solutions. Although the band maxima of the L_1 absorption bands for reactant and product are shifted by only about 25 nm, γ is large at 580 nm since this wavelength lies on the still descending portion of the product L_1 band but is at the minimum between the tail of the L_1 band and the onset of the doublet absorption band for $Cr(en)_3^{3+}$.

10. E. Jorgensen and J. B. Bjerrum, *Acta Chem. Scand.*, **13**, 2075 (1959).

Figure legends.

Figure 1. Block diagram of the apparatus. The amplified, frequency doubled Nd glass laser (Korad Co.) produces up to 1.5 J, 20 nsec pulses at 530 nm. The irradiated volume is approximated 2x2x9.5 mm; the monitoring beam scans the first 2 mm depth of solution, the solution path being 9.5 mm. The tracing of an oscilloscope photograph shows photoproduct formation for 0.2M $[\text{Cr}(\text{en})_3](\text{ClO}_4)_3$ in 1×10^{-2} M HClO_4 (twice filtered through 0.22 μm Millipore filters--dust produces large monitoring beam disturbances). The upper trace (10 mV/div., 2 $\mu\text{sec}/\text{div.}$) shows the transmitted monitoring beam intensity (each division representing 8% transmitted light. The lower trace, (100 nsec/div) shows the photodiode signal; the pulse was ca 1 J. See also Refs. 4c and 11.

11 A. R. Gutierrez and A. W. Adamson, *J. Phys. Chem.*, submitted.

Figure 2. Excited state diagram for a d^3 system.

Figure 3. Rate constant for delayed product grow-in, \bullet , and τ^{-1} for D_1° emission, Δ . Apparent activation energy is 10 kcal/mole.

Fig 1

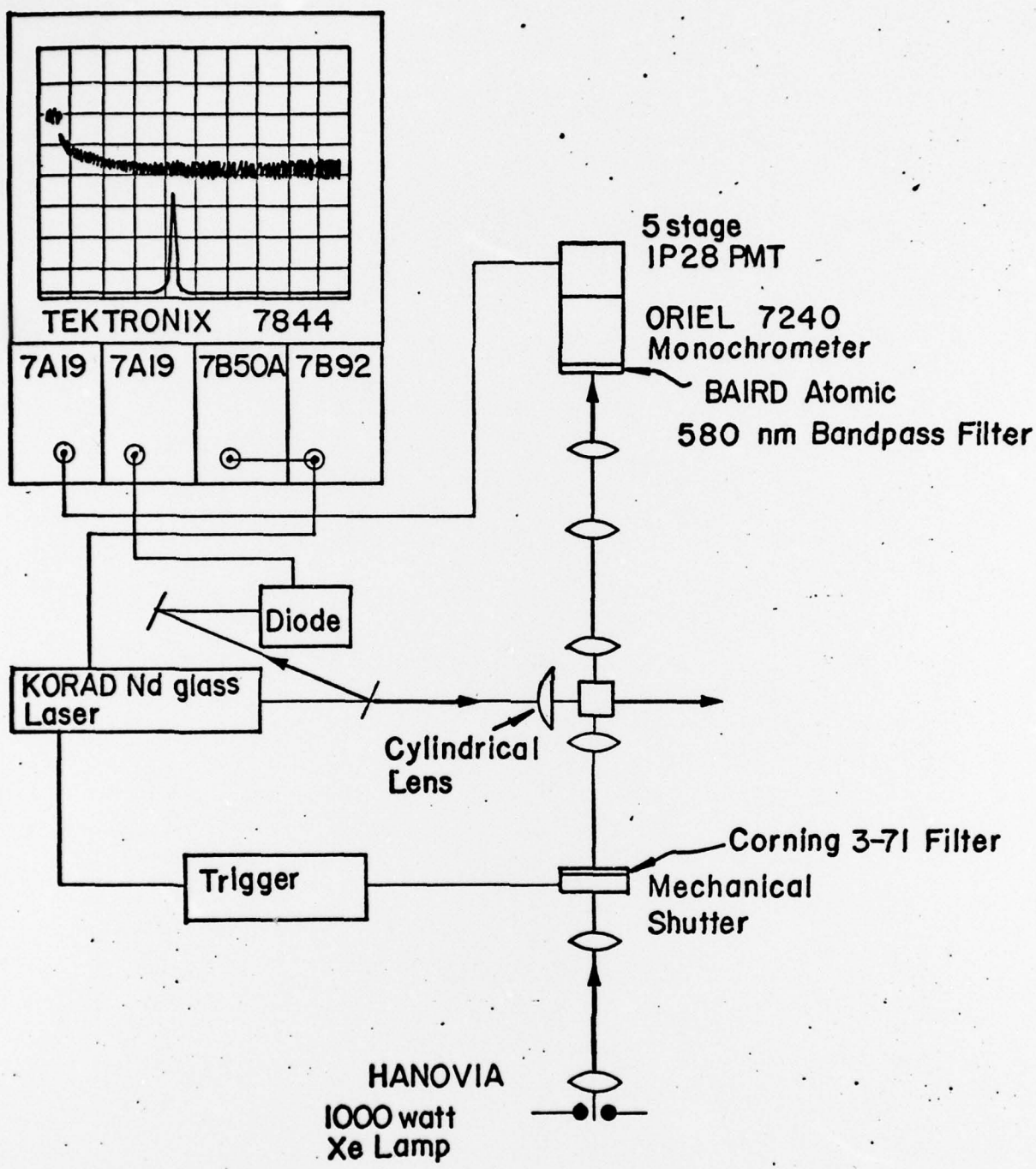


fig 2

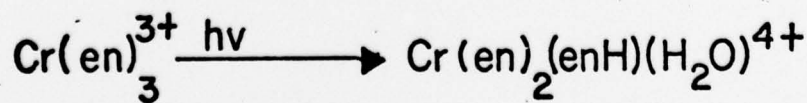
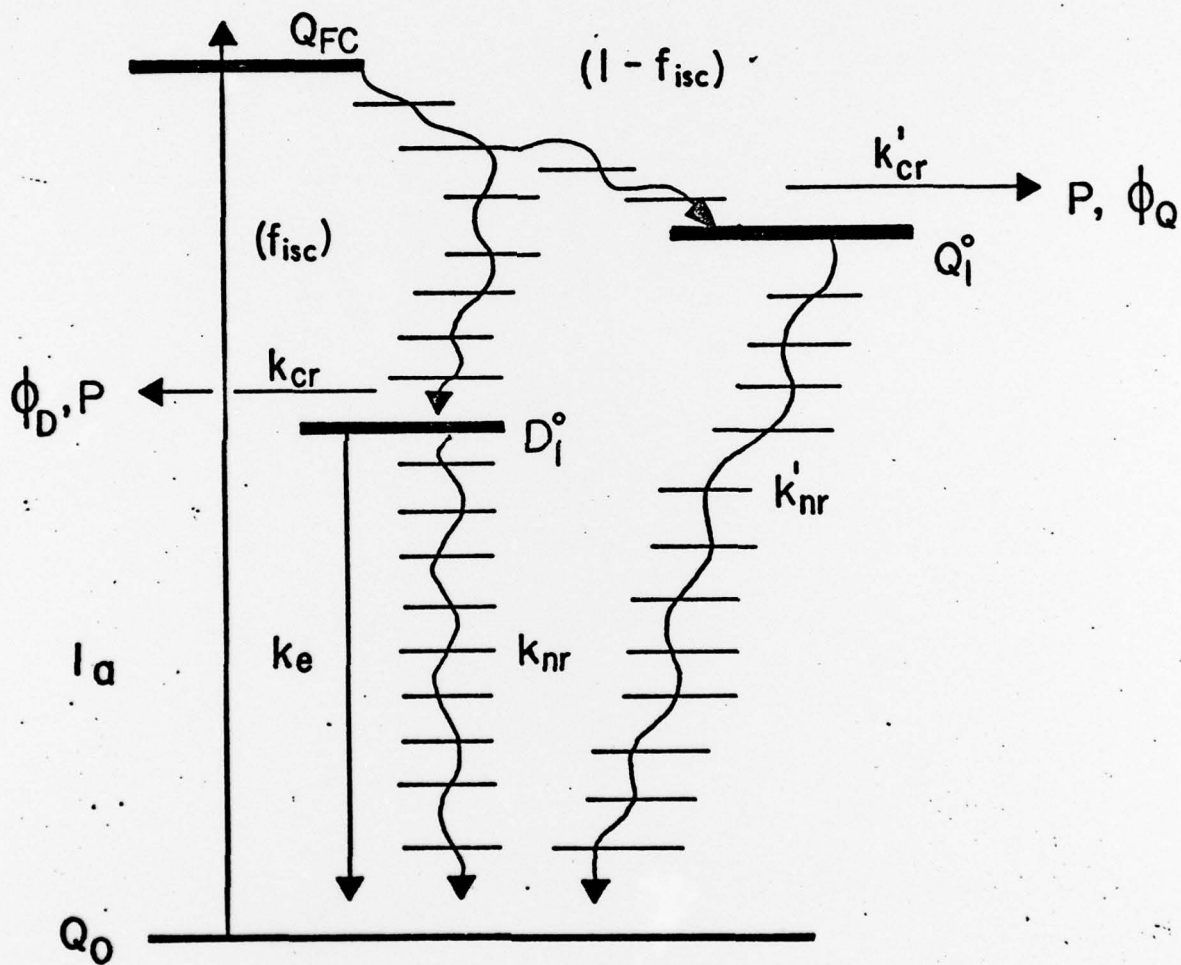
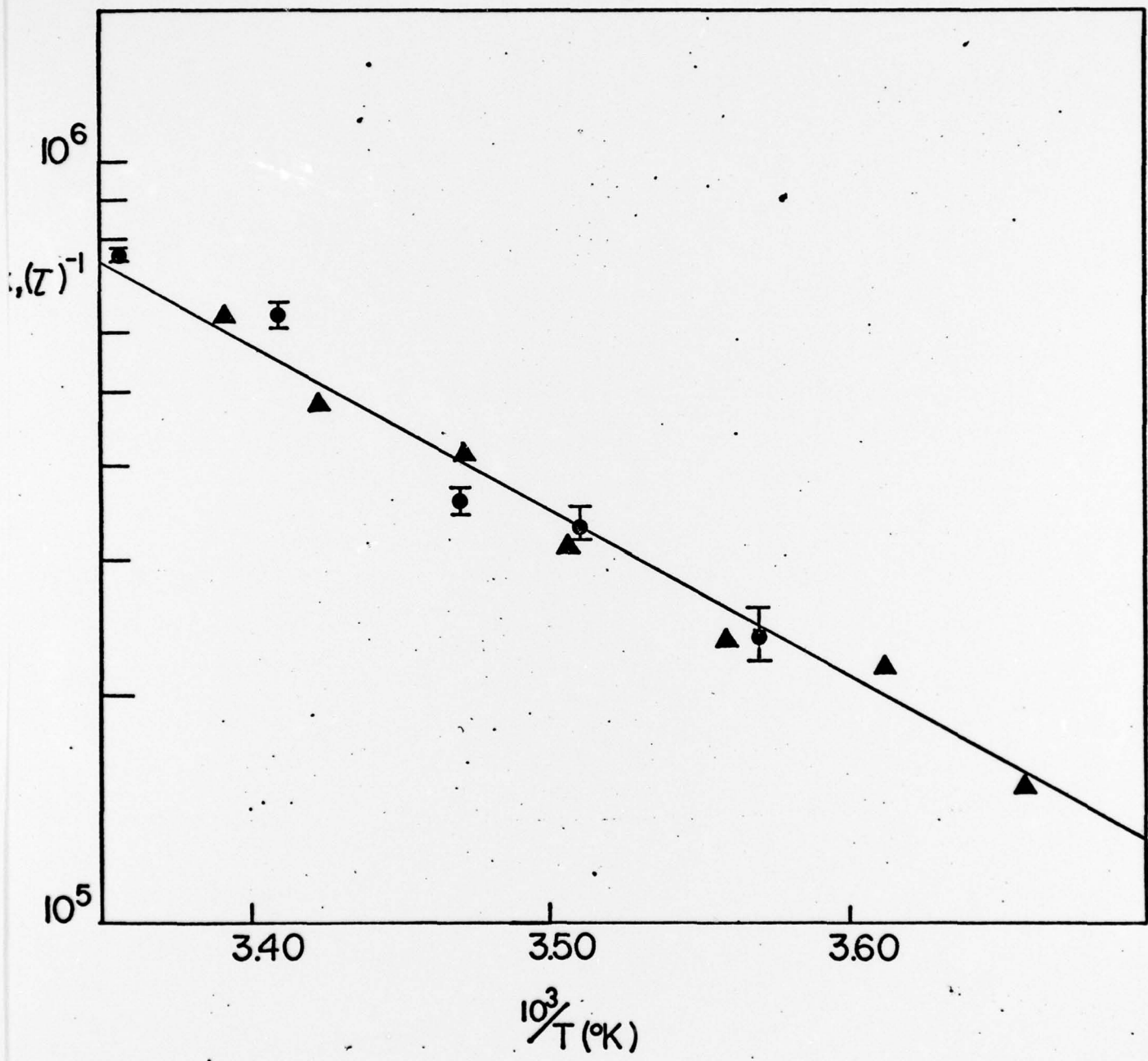


Fig 3



TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP 1	6	U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1		

TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1	Dr. G. B. Schuster University of Illinois Chemistry Department Urbana, Illinois 61801	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	1	Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah	1
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1	Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. M. H. Chisholm Princeton University Department of Chemistry Princeton, New Jersey 08540	1	Dr. M. Rauhut American Cyanamid Company Chemical Research Division Bound Brook, New Jersey 08805	1
Dr. J. R. MacDonald Naval Research Laboratory Chemistry Division Code 6110 Washington, D.C. 20375	1		